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# **REVERSE OSMOSIS PROCESSING OF ORGANIC MODEL COMPOUNDS AND FERMENTATION BROTHS**

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# Reverse osmosis processing of organic model compounds and fermentation broths

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## Abstract

Post-treatment of an anaerobic fermentation broth was evaluated using a 150 gal/day, single cartridge prototype reverse osmosis (RO) system. Baseline tests were conducted at 25 °C using six organic model compounds representing key species found in the fermentation broth: ethanol, butanol, acetic acid, oxalic acid, lactic acid, and butyric acid. Correlations of the rejection and recovery efficiencies for these organic species, individually and in simulated mixtures, were obtained as a function of feed pressure with and without recirculation of the retentate. The actual fermentation broth obtained from a continuous-flow biohydrogen process was treated by the RO system under the operating conditions similar to those used in the baseline tests, resulting in greater than 95% removal of total organic carbon. These results are encouraging and useful for further studies on the feasibility of incorporating the RO technology into an integrated and field deployable wastewater management and water recovery system.

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**Keywords:** Water reclamation; Waste management; Biohydrogen; Fermentation broth; Reverse osmosis

## 1. Introduction

Water is an essential and high-volume logistical materiel for military operations involving long duration human settlement in isolated areas, such as deployed airbases, where self-sufficiency is required to minimize airlift for non-weapon supplies. At the same time, wastewaters generated from living quarters must be effectively managed to maintain sanitary conditions at the operation facilities. These requirements necessitate the development of effective and deployable waste management and resource recovery systems. According to findings from independent field studies, the wastewaters (blackwater and graywater) contribute to about 93% by weight of the total wastes generated at deployed airbases. Since these wastewaters consist of primarily water (>99.5% by weight), it is of the highest interest and priority to develop compact and robust systems to

reclaim water from these wastewaters. The reclaimed water is needed as a supply for a variety of potential uses including showers, laundry, drinking, vehicle washing, and dust control.

One of the technology development areas currently being pursued at Air Force Research Laboratory (Tyndall AFB, FL) involves biohydrogen production via dark anaerobic fermentation of waste streams generated from deployed air base operations. The dark anaerobic fermentation approach presents the most plausible near-term opportunities for practical biohydrogen production (Bene-mann, 2001). The fermentation broth resulting from the biohydrogen process contains a variety of suspended and dissolved organic and inorganic compounds that must be removed for water recovery and reuse. The dissolved organic species typically include C1 to C6 mono- or dicarboxylic acids (in both salt and acid forms) and alcohols (Lay et al., 1999; Chen and Lin, 2003; Valdez-Vazquez et al., 2005). In biohydrogen production experiments conducted in the batch mode, total organic carbon (TOC) of

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the fermentation broth was typically as high as 20,000 mg/L. Of this TOC total, the volatile acids and alcohols contribute about 30% and 10%, respectively. The other 60% of the TOC is likely to be suspended solids, such as residual organic nutrients and microbial cell mass. TOC concentration of the fermentation broth obtained from continuous-flow experiments was about one third of that found in the batch experiments, and displayed variations in the distribution of the acids and alcohols. Therefore, the fermentation broth from the microbial hydrogen production processes may not be dischargeable nor reusable without post-treatment to remove suspended and dissolved solids, particularly organic species.

Reverse osmosis (RO) is a relatively mature technology that is widely used for desalination and water purification applications. RO was initially demonstrated and intended to be used for desalination of seawater to produce freshwater in the 1950s (Sourirajan, 1970). Today, there exist many large-scale desalination plants based on the RO technology. RO can achieve over 99% removal efficiency for sodium chloride and most other inorganic compounds found in seawater. In addition to the vast literature coverage on electrolyte (i.e., inorganic and organic acid salts) removal from water, there is a new trend aimed at broadening the range of RO applications. One specialty area involves separation of organic mixtures. Specifically, state-of-the-art RO membranes are capable of partitioning small organic compounds, such as ethanol. This ability of RO membranes has been applied to remove alcohol from distilled spirits without affecting the sensory properties (Rohmann, 1991; Bujake, 1998). A recent study by Ozaki and Li (2002) has evaluated a number of small organic molecules, particularly acids and alcohols containing four carbons or less, and reported that rejection of these compounds is a strong function of the molecular size. Similar studies on carboxylic acid mixtures were reported by other researchers (Todtheide et al., 1997; Ragaini et al., 2004). Since the RO system is simple, compact, and light-weight, it is an attractive water purification option for applications where space and logistics are of primary concern. NASA has shown great interest in and has considered the RO technology as one of the key elements in its Water Recovery and Management System (WRMS) for long-duration space missions. Tansel et al. (2005) evaluated the feasibility of the sequential membrane filtration approach for treatment of the effluent from an aerated rotating membrane bioreactor system (ARMS), and reported that both the solids removal and flux of the RO membrane were significantly affected by the effluent quality from the prefilter.

Experimental investigation of separating organic species from aqueous mixtures by RO has been complemented by many ongoing modeling efforts. A recent study by Lee and Lueptow (2001) has developed a simple transport model based on the solution-diffusion model incorporating concentration polarization and RO membrane properties. Similarly, a mass transfer model based on the Kimura–

Sourirajan Analysis was developed for separating aqueous organic multi-component solutions by RO (Weissbrodt et al., 2001). This model describes the mass transport through RO membranes and enables the prediction of the retention behavior of organic multi-component solutions. Because many of the simplifications in the classical theory for the solution-diffusion mechanism become inappropriate for separation of aqueous solutions of organic molecules, the classical solution-diffusion theory for modeling RO systems was recently reformulated (Paul, 2004).

The purpose of this study was to demonstrate the feasibility of the RO technology for water reclamation from the anaerobic fermentative biohydrogen production broth, and provide preliminary engineering design data for process scale-up and integration calculations. This study focused on correlating effects of two process control parameters (i.e., feed pressure and retentate recirculation) on rejection of selected model compounds (either as a single component or as a simulated mixture) and recovery of the permeate. RO performance tests were also conducted using an actual fermentation broth obtained from an on-site, bench-scale biohydrogen production reactor system. Similar technical approaches have recently been validated for aerobic bioconversion of wastewater followed by RO treatment step for water recycling in electronic industry (Chen and Chen, 2004), meat processing industry (Bohdziewicz and Sroka, 2005), and long duration space missions (Tansel et al., 2005). Results reported in this paper would be a useful addition to this newly proposed resource recovery tool involving bioconversion/RO reclamation.

## 2. Methods

### 2.1. Materials

An actual fermentation broth was collected over a two-week period from an on-site, continuous-flow biohydrogen reactor, and the effluent sample was transferred twice daily to a holding tank placed in a refrigerator. The bioreactor was fed with a simulated kitchen waste comprising potato (cooked by a microwave), bread and pork and beans (canned) well mixed with a blender, and mixed with water to decrease the viscosity of the solution. Total suspended solids (TSS) of the paste were about 10%. Tap water was added with a dilution factor of 30:1, and the diluted suspension was pumped into the bioreactor at a predetermined flow rate. This feed stream had a pH value of about 6. The fermentation process typically reduced the volume of TSS by 60%. The remaining TSS in the fermentation broth was collected in a holding tank placed in a refrigerator, and kept unstirred to allow particulates to settle. The supernatant liquid in the holding tank was transferred into the feed tank of the RO system prior to the RO experiment.

Ethanol, butanol, acetic acid, lactic acid, oxalic acid and butyric acid were used as model compounds in this study. The rationale for selecting these compounds was provided

in Section 3. These chemicals (Aldrich Chemical Co., ACS grade) were used as received.

## 2.2. Apparatus

Fig. 1 is a schematic flow diagram of the test apparatus, which was based on a commercial saltwater series reverse osmosis system (Crane Environmental Model EPRO 150SW) with minor modifications. The unit was equipped with a thin film composite polyamide RO membrane (Dow Chemical Co. FILMTEC FT30) in a single-pass configuration and with a 1.5 HP stainless steel high-pressure pump. The unit had a capacity rating of 150 gal/day at 1000 psig. Factory specified single-pass recovery for this RO system was 5%. Since the recirculation of a portion of the retentate can enhance RO system performance (Gonzalez et al., 2002), a recirculation loop was added to evaluate the improvement on the recovery of permeate and the rejection of the selected model compounds and fermentation broth. A low-pressure diaphragm pump (SHURflo® Multi-Purpose 115V, 3.3 GPM at 45 psig) was also added to pump the feed stream through the prefilter (Flow Max, Model FM-5-975, 5  $\mu$ m pore size), and maintain a minimum inlet pressure of 20 psig and a feed flow rate of 0.2 gal/min (GPM) for the high-pressure feed pump. Recirculation of a portion of the feed stream was also tested to decrease the demand on the feed stock volume required for each experiment. The RO unit was equipped with an in-line total dissolved solids (TDS) meter (Hanna TDS Controller, Model HI 983329) to measure the conductivity of the permeate, and display the calculated TDS value in ppm (mg/L), based on the correlation of TDS with dissolved NaCl since the system was originally designed for seawater applications. The displayed TDS values were recorded during the course of each experiment. Since no calibration of the TDS meter with the concentrations of dissolved species in

the simulated and actual fermentation broths, was attempted, the TDS reading was only used to indicate system stability. For deionized water, the TDS reading was 3 ppm (baseline), and for sample solutions the TDS reading ranged between 30 and 200 ppm depending on the type and concentration of the species involved. Sample collections began after the TDS reading had become stable, suggesting that the RO system reached a steady-state.

## 2.3. Analyses and measurements

Concentrations of organic acids, alcohols, and total organic carbon (TOC) in each sample collected from the RO experiments were quantified. The pH and the volumetric flow rate of each stream (feed, permeate, and retentate) were also measured.

Alcohols (ethyl, propyl, and butyl alcohols) were analyzed using an HP 5890 Gas Chromatograph (GC) with an FID detector. A 1.83 m  $\times$  0.318 cm packed stainless steel column with Poropak S packing (Supelco P/N 20336) was used. The GC was operated isothermally at 155  $^{\circ}$ C, an inlet temperature of 175  $^{\circ}$ C, and a detector temperature of 250  $^{\circ}$ C. Helium (ultra high purity) was used as the carrier gas at a flow rate of 30 mL/min. Sample injection volumes were 1  $\mu$ L and the run time was ten minutes.

Organic acids were analyzed using a Dionex DX 500 Ion Chromatograph (IC) with a conductivity detector and a Dionex AS40 Auto Sampler. The detector was equipped with a Dionex AMMS-ICE II anion micro-membrane suppressor and 5 mM tetrabutylammonium hydroxide was used as the regenerant. The eluent was 0.4 mM heptafluorobutyric acid at a flow rate of 1.5 mL/min. The instrument used a Dionex Ion Pac ICE-AS6 column packed with moderately hydrophobic resin functionalized with sulfonic acid and carboxylic acid groups. TOC of the fermentation broth

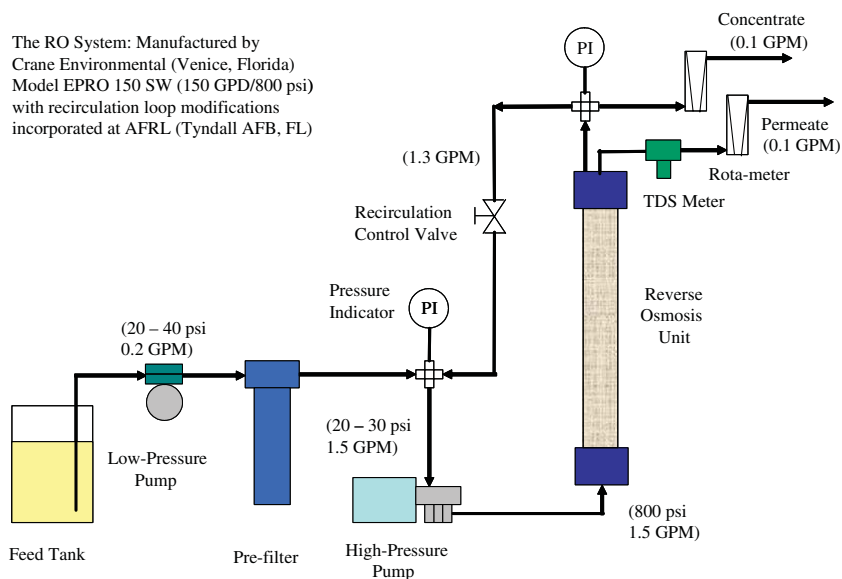


Fig. 1. Process flow diagram of the RO test unit.

was measured using a Total Organic Carbon Analyzer (Shimadzu Model TOC 5000A) with a Shimadzu ASI-5000A Auto Sampler. The instrument used oxygen (ultra high purity) at a flow rate of 150 mL/min. The fermentation broth samples for both TOC and IC analyses were first centrifuged at 10,000 rpm for 5 min. For each sample, a volume of 1 ml of the supernatant was taken and diluted 100 times with DI water. For IC analysis, 0.5 ml of the diluted sample solution was transferred into an Auto Sampler vial equipped with a filter cap (Dionex PolyVial, P/N 038011). For TOC analysis, 5 ml of the diluted sample solution was drawn into a plastic syringe and filtered through a cartridge filter (Lida Manufacturing Corp. 0.45  $\mu$ m hydrophilic cellulose acetate membrane) into a TOC sample vial.

The pH was measured with a pH/ion meter (Accumet Model 25) equipped with an Orion pH probe. TDS readings displayed on the in-line TDS meter (the permeate stream) were recorded in all experiments.

The volumetric flow rates of the permeate and the retentate were measured by determining the amount of time used to fill a 1 L graduated cylinder with the respective streams. These measurements were taken prior to collecting samples from the permeate and retentate streams. The volumetric flow rate of the feed was calculated by adding the measured permeate and retentate flow rates.

#### 2.4. RO performance calculations

The terminology used in this paper is summarized below, referring to Fig. 1 for the actual locations of each stream:

Feed—the stream entering the RO system via the high-pressure feed pump;  
 Permeate—the stream passing through the RO membrane (also known as filtrate); and  
 Retentate—the stream rejected by the RO membrane (also known as concentrate, or reject).

The following two parameters were calculated from data generated from each RO experiment:

$$\% \text{ Recovery} = \frac{(\text{permeate\_flow\_rate})}{(\text{feed\_flow\_rate})} \times 100\%$$

$$\% \text{ Rejection} = \frac{(\text{feed\_concentration} - \text{permeate\_concentration})}{(\text{feed\_concentration})} \times 100\%$$

### 3. Experimental section

#### 3.1. Selection of model compounds and simulated mixtures

This study was intended to evaluate the ability of the seawater RO membrane to remove TDS from a series of individual organic model compounds, and simulated and

actual fermentation broths. The performance of the RO membrane was described in terms of TOC concentration of the broth or mass concentration of individual components. Based on preliminary IC and GC analyses, a number of dissociated (ions) and dissolved (free acids, alcohols, and other water-soluble compounds) organic and inorganic species were identified as key contributors to the TDS in the fermentation broth derived from the biohydrogen production process. The compounds identified in this study were consistent with those organic acids and alcohols that have been well documented as byproducts of dark fermentation for hydrogen production in the literature. The key acids and alcohols identified in the fermentation broth obtained from batch and continuous-flow biohydrogen production experiments and their typical concentrations are shown in Table 1. These include acetic acid, oxalic acid, lactic acid, butyric acid, ethanol, and butanol. Formic acid, malonic acid, propionic acid, succinic acid, and propanol were also detected, but their concentrations were typically less than 100 ppm. Table 1 also shows concentrations of six organic model compounds that have been chosen to closely match those of their counterparts found in the fermentation broth.

The fermentation broth obtained from batch biohydrogen production experiments typically contained 20,000 mg/L TOC, of which 40.6% was accounted for from the six key components. Furthermore, a TDS value of 4.3 wt% can be estimated for this broth by the total concentration of the six components divided by 40.6%. The fermentation broth derived from batch-fed, continuous-flow experiments showed a lower TOC of about 6400 mg/L. The six key components contributed 35.8% of the TOC. Similarly, a TDS value of 1.4 wt% can be derived for this broth. In addition to the large variations in the total concentration, the distributions of the six components in both cases were noticeably different. For example, the fermentation broth from the batch tests contained much higher concentrations of oxalic and lactic acids. Since the continuous-flow conditions would reflect the eventual mode of operation for a field fermentation/RO system, the concentrations for the six model compounds were selected based on the typical continuous-flow test data, and the analysis of the actual fermentation broth used for the RO experiments.

Two simulated fermentation broths were studied. The first simulated broth was a mixture of ethanol and acetic acid, while the second one was a mixture of all six model compounds. Ethanol and acetic acid represent the most important by-products from the dark fermentation process for hydrogen production. They are also smallest in terms of molecular weights and sizes among the components in the fermentation broth, and therefore are most difficult to be removed from the solutions by RO. The second mixture was selected to simulate more closely to the composition of the fermentation broth. In both cases, concentrations of individual components in each mixture were measured, and rejection was calculated for each component and integrated for the given mixture.

Table 1  
Typical compositions of fermentation broths and selection of model compound concentrations in simulated mixture

Parameter	Unit	Acetic Acid	Oxalic Acid	Lactic Acid	Butyric Acid	Ethanol	Butanol	Sum	Total	Accountables (% Total)
MW	(g/mol)	60.05	90.04	90.08	88.11	46.07	74.12			
No. of Carbon		2	2	3	4	2	4			
<i>Batch tests</i>										
Average concentration in fermentation broth	(mg/L)	4000	1500	4000	4000	2000	2000	17500	43100	40.6
	(mmol/L)	66.6	16.7	44.4	45.4	43.4	27.0	243.5		
	(mmol-C/L)	133.2	33.3	133.2	181.6	86.8	107.9			
	(mg TOC/L)	1599	400	1599	2179	1042	1295	8113	20000	40.6
<i>Batch-fed continuous-flow tests</i>										
Average concentration in fermentation broth	(mg/L)	2400	250	550	1300	350	220	5070	14200	35.8
	(mmol/L)	40	3	6	15	8	3	75		
	(mmol-C/L)	79.9	5.6	18.3	59.0	15.2	11.9			
	(mg TOC/L)	959	67	220	708	182	142	2279	6360	35.8
Six-component simulated mixture concentration	(mg TOC/L)	1000	70	220	708	182	143	2323		
	(mmol-C/L)	83.3	5.8	18.3	59.0	15.2	11.9			
	(mmol/L)	41.7	2.9	6.1	14.8	7.6	3.0	76		
	(mg/L)	2502	263	550	1300	349	221	5261		

### 3.2. Selection of test conditions

Table 2 summarizes all RO experiments performed in this study. The concentrations of the individually tested model compounds ranged from 3000 mg/L (0.3 wt%) to 13,000 mg/L (1.3 wt%). The concentrations of these model compounds in the simulated mixtures ranged from 50 to 1750 mg/L, which were selected to match the concentrations of the corresponding components in the actual fermentation broth. The simulated feed stream had a total (i.e., sum of all components) concentration of 4600 mg/L as compared to 4200 mg/L for the fermentation broth. Single component feed solutions and simulated mixtures were prepared in 20 L batches according to the component concentrations given in Table 2. Deionized (DI) water was used as the balance for all feed solutions.

Three feed pressures ranging from 0.83, 2.8, 5.5 MPa (120, 400–800 psig) were used in this study. These pressures were selected primarily to overcome the osmotic pressure of the solution, which can be either measured experimentally or estimated from known correlations. However, no experimental osmotic pressure data for the selected six

model compounds were found through extensive literature searches. Since the fermentation broths contained relatively high TDS values (1.4 and 4.3 wt% for continuous-flow and batch experiments, respectively), estimation of osmotic pressure, which is applicable for diluted solutions, could not be used. According to literature, the osmotic pressure for NaCl–water solution is 398 psia at 3.39 wt% of NaCl (typical seawater concentration) and 534 psia at 4.47 wt% of NaCl (Sourirajan, 1970). Assuming the osmotic pressure for the fermentation broth can be approximated by that of NaCl at corresponding TDS concentrations, the pressures of 400 and 800 psig would be adequate to overcome the osmotic pressure of the test solutions, particularly those derived from the continuous-flow experiments. The low pressure at 120 psig was selected to study the trade-off between RO performance and energy consumption.

Since RO performance, in terms of permeate flux, can be affected by the temperature of the feed stream (Goosen et al., 2002; Agashichev and Lootah, 2003), the temperature of feed solutions was monitored in each experiment. As recently reported by Goosen et al. (2002), the permeate flux increased with increasing feed temperature. The

Table 2  
Test matrix for RO processing of model compounds and fermentation broths

Test series	Temperature (°C)	Ethanol (mg/L)	Butanol (mg/L)	Acetic acid (mg/L)	Lactic acid (mg/L)	Oxalic acid (mg/L)	Butyric acid (mg/L)
Single component, w, w/o recirculation	25	3000–13,000					
Single component, w, w/o recirculation	25		5000–6000				
Single component, w, w/o recirculation	25			4000–10,000			
Single component, w/o recirculation	21				3000		
Single component, w/o recirculation	21					3000	
Single component, w/o recirculation	21			7000			
Simulated Broth#1, w/o recirculation	22	3900		2100			
Simulated Broth#2, w/o recirculation	21	250	150	1400	1100	60	1600
Fermentation Broth, w/o recirculation	25	350	50	1650	300	–	1750

Note: All test sets, except for the fermentation broth experiment, were conducted at three system pressures of 0.83, 2.8, 5.5 MPa (120, 400, 800 psig), respectively. The fermentation broth experiment was conducted at 5.5 MPa (800 psig).

increase in permeate flux was less than 10% when the temperature rose from 20 to 30 °C, whereas the permeate flux nearly doubled when the temperature rose from 30 to 40 °C. As is known in the literature, the optimal operating temperature for the anaerobic biohydrogen fermentation process involving *Clostridium* sp. is 37 °C (Yokoi et al., 2001; Sung et al., 2002), although the process can be operated at room temperature with a slower rate of hydrogen production. The solutions used in this study were prepared and stored at room temperature ranging from 21 to 25 °C. All RO experiments were conducted at room temperature, without any form of thermal control, except for the actual fermentation broth, which was refrigerated during the two-week collection period at 4 °C. The supernatant was warmed up to the room temperature after it was transferred to the feed tank. These room-temperature experiments would provide more conservative RO performance results.

All feed solutions were prepared without pH adjustments. For lactic acid ( $pK_a = 3.08$ ) and oxalic acid ( $pK_{a1} = 4.19$ ,  $pK_{a2} = 1.23$ ), pH of the feed solution is lower than that of acetic acid ( $pK_a = 4.75$ ) and butyric acid ( $pK_a = 4.81$ ). Rejection is shown to be a strong function of pH for organic acids (Ozaki and Li, 2002). The undissociated acids appear to have smaller molecular diameters than those of dissociated species, particularly if metal cations are present as the counter ions. When pH of an acid solution is raised to the neutral level by adding a base, the rejection shows a considerable increase. For example, the rejection of acetic acid is increased from 35% at pH of 3 to 70% at pH of 5.5, and to >99% at pH of 9 (Ozaki and Li, 2002). In addition, further lowering pH may have caused slight shifts of the dynamic boundary layer at the membrane interface. Since the fermentative biohydrogen process is optimally operated at a pH value of about 5.5, the organic acids produced by the microbes as byproducts of hydrogen production must be neutralized by addition of caustic materials into the fermenter. As a result, the fermentation broth contains high concentrations of metal ions. This highly dissociated electrolyte solution would be in favor of water reclamation by the RO process.

The addition of a second solute may affect the rejection of the first solute in a solution. If the rejection of the first solute is enhanced, the presence of the second solute is said to have a positive alteration of rejection of the first solute, whereas if the rejection of the first solute is decreased, the presence of the second solute results in a negative alteration. Both positive and negative alterations of rejection were reported for multi-component systems containing carboxylic and dicarboxylic acids (Laufenberg et al., 1996; Todtheid et al., 1997).

### 3.3. RO system operating procedures

To operate the system, the pre-filtration (low-pressure) pump as shown in Fig. 1 was first turned on to ensure the suction line of the high-pressure feed pump was flooded

at a pressure ranging from 20 to 45 psig, required for the high-pressure feed pump to function properly. The system was allowed to pump for five minutes, and the initial permeate and retentate streams were discharged to minimize potential cross contamination from previous trials. Once the RO system was flushed, the permeate and retentate streams were recycled back into the feed tank to preserve materials. Pressure head at the pump discharge was maintained by restricting the flow of the retentate stream through a metering valve (Hexvalve Model HN39F-4-P). The system pressure was steady throughout each experiment.

The TDS controller was monitored for changes. Once the reading on the meter stopped changing, the system was at steady state and was ready for sampling. The flow rates of the permeate and the retentate streams were measured using the methods described previously. Samples of these streams and the feed solution were then collected. Typically, 25 mL of each aqueous sample was used for analyses including the measurement of pH and quantification of concentrations by IC and GC.

Since the same RO membrane was used in all experiments, after each experiment, 20 L of DI water were pumped through the RO system at a pressure of 300 psig to flush out the residue retentate and permeate streams. The water flush appeared to thoroughly clean the RO membrane as reflected by TDS meter readings being returned to the normal baseline level of 3 ppm.

## 4. Results and discussion

Experimental data were analyzed and presented in terms of permeate flux, rejection and recovery without and with recirculation of the retentate. Correlations of each of these parameters with respect to feed pressure, recirculation, and feed concentration were developed. Fig. 2 shows the effect of feed pressure on the rejection of individual organic species without recirculation of the retentate stream. In general, the rejection of each model compound increased by

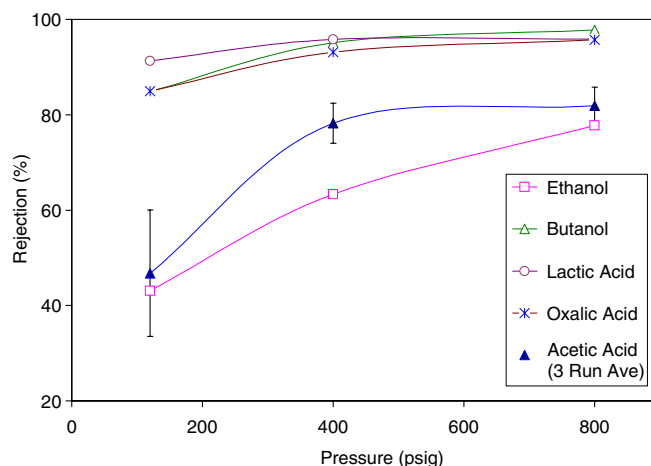


Fig. 2. Rejection of organic model compounds.

elevating the feed pressure. Multiple experiments using acetic acid were conducted to establish the repeatability of the RO test setup and procedure. Specifically, three separate RO experiments were conducted with acetic acid feed concentrations of 4200, 5000, and 7200 mg/L. Rejection of acetic acid averaged over the three experiments increased from  $46.8 \pm 13.3\%$  at 120 psig,  $78.2 \pm 4.18\%$  at 400 psig, to  $81.9 \pm 3.88\%$  at 800 psig. At 120 psig, the rejection of acetic acid was relatively low and appeared to have a large standard variation. The performance of the high-pressure pump was relatively unstable at 120 psig, since the RO system was designed to be operated at 800 psig. At the operating pressure of 120 psig, the high-pressure pump appeared to be relatively sensitive to the flow/pressure fluctuation in the low-pressure pump. More detailed discussion on this issue is provided in the section addressing the recovery results (Fig. 3). At higher pressures, however, the rejection of acetic acid was nearly doubled with standard deviations of less than 5%. Furthermore, these three experiments involving acetic acid were conducted on separate dates that were far apart (4 months) and between these dates, the RO system was used to run experiments involving other model compounds. It is therefore suggested that the effect of residue solute in the RO system, if at any measurable level, was negligible for the purpose of this study.

The rejection of alcohols, particularly ethanol, was also effected by pressure. Ethanol is especially difficult to separate from water using RO due to its small molecular size (Bujake, 1998). As shown in Fig. 2, increasing the feed pressure from 120 to 800 psig enhanced the rejection of ethanol from 43% to 78%. Butanol, due to its larger molecular size, was effectively rejected at low pressures. The rejection of butanol reached 85% at 120 psig, and steadily increased to 98% at 800 psig. The rejection of butanol was not as sensitive to feed pressure as those of ethanol and acetic acid. Similarly, the rejection of lactic acid and oxalic acid were high and relatively unaffected by the feed pressure. These trends could also be explained as a phenomenon due to

the level of osmotic pressure of a given compound. Acetic acid and ethanol may have higher osmotic pressures than the other model compounds. If the osmotic pressure is between 120 and 400 psig, a large increase in rejection of the solute would be expected with increasing pressure from 120 to 400 psig.

The flux of water across the membrane is a strong function of the differential pressure between the feed pressure and the osmotic pressure of the solution. As shown in Fig. 3, the recovery increased linearly with feed pressure in the entire range tested for three individual species without recirculation of the retentate. Although the recovery of permeate from the butanol solution showed a slightly lower slope as compared to those of ethanol and acetic acid, this variation was within the margin of errors ( $\pm 4\%$ ) as discussed for the acetic acid experiments. Fig. 3 also compares recovery data derived from RO experiments with recirculation of the retentate. At 120 psig, the recovery appeared to have a highest percentage increase. However, it was determined that at this low pressure, performance of the high-pressure pump was extremely sensitive to the feed flow rate and pressure build-up generated by the low-pressure pump. Due to occasional on-off oscillation of the low-pressure pump triggered by over-pressure (45 psig), a diversion line was added between the low-pressure pump and the high-pressure pump. One RO experiment using ethanol was performed at 120 psig prior to the diversion line modification. Results from this set of experiments show a linear increase (dotted line in Fig. 3) with feed pressure, similar to those without recirculation. However, the recovery increased at a steeper slope with the recirculation as compared to that without recirculation of retentate. At 800 psig, the recovery reached about 35%, as compared to the single pass recovery of 5% specified by the manufacturer of the RO system. Fig. 4 shows the effect of recirculation on rejection, as compared to the rejection of the solutes without recirculation. At 120 psig, the performance of the high-pressure pump was unstable as discussed previously, and a significant

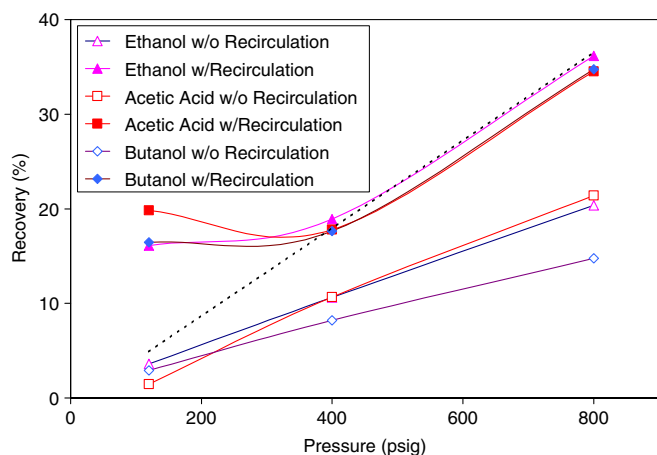


Fig. 3. Recovery of permeate for organic model compounds with and without recirculation of retentate.

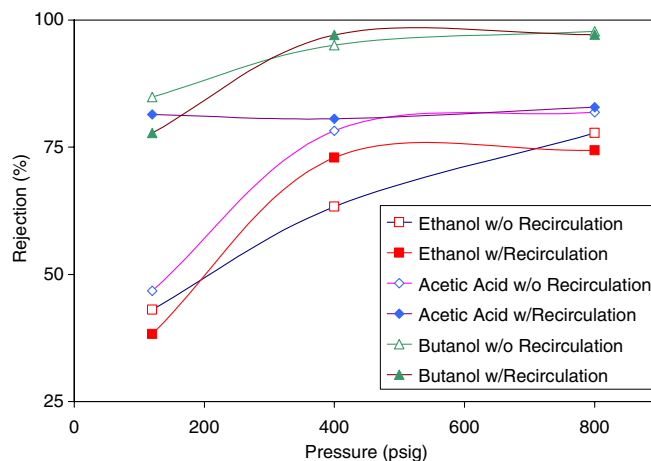


Fig. 4. Rejection of organic model compounds with and without recirculation.

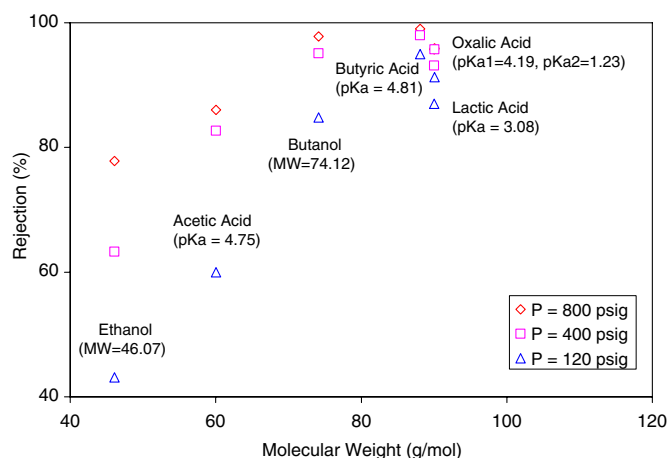


Fig. 5. Correlation of rejection with molecular weights of model compounds.

increase in rejection was particularly shown in the case of acetic acid. At 400 and 800 psig, recirculation of retentate did not appear to affect the performance of the membrane and its ability to reject the selected organic model compounds.

Fig. 5 shows the effect of rejection versus molecular weight of the selected model compounds at three different pressures. The rejection increased linearly with increasing molecular weight from ethanol (46.07) to butyric acid (88.11) at all three pressures (120, 400, and 800 psig). This observation was consistent with other reported correlations involving molecular weight and functionality of organic compounds (Ozaki and Li, 2002; Todttheide et al., 1997). Both lactic acid (90.08) and oxalic acid (90.04) showed slightly lower rejection. This slight variation may be contributed to the extent of ion dissociation, stereo structure of the molecule, and affinity to the membrane which have been suggested in the literature (Ozaki and Li, 2002).

As for the results of the rejection of individual species obtained from experiments involving the fermentation broth and simulated mixtures, the rejection of each species in both cases followed similar trends with increasing pressure as those observed in the baseline experiments where measurements were made for each component individually. However, the level of rejection for each species was increased when the feed stream was either the fermentation broth or the simulated mixture, as compared to the feed stream of a single component. Figs. 6 and 7 show the RO performance for ethanol and acetic acid, respectively, as single-component solutions and simulated mixtures. The two-component (simulated broth 1) and six-component (simulated broth 2) mixtures are defined in Table 2. As shown in Fig. 6, the rejection of ethanol increased steadily from the single-component solution, to the two-component mixture, and to the six-component mixture, while the recovery of permeate remained relatively unchanged. As for the pressure dependency, the rejection increased 20% at 120 psig, and about 10% at 800 psig, as compared to the single-component ethanol solution. The rejection

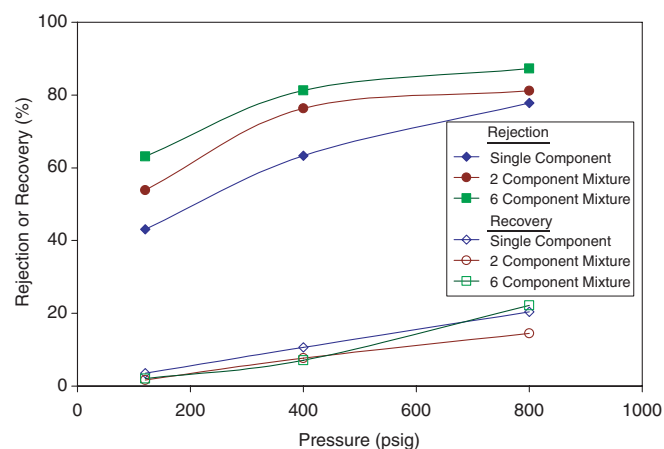


Fig. 6. Comparison of RO performance for ethanol between single-component solution and simulated broths.

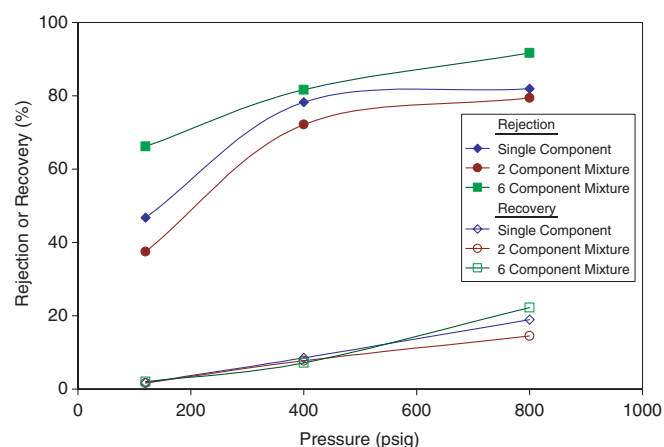


Fig. 7. Comparison of RO performance for acetic acid between single-component solution and simulated broths.

of acetic acid displayed a similar trend in terms of rejection and recovery, as shown in Fig. 7. However, the single-component solution experiment appeared to show higher rejection than the two-component mixture. As shown in Fig. 2, the data points for the single-component acetic acid solution are averaged values based on three separate experiments. Based on the given standard deviations, the data derived from the single-component and two-component mixture appeared to be within the experimental errors. The rejection of acetic acid from the six-component mixture clearly increased over the pressure range. All RO experiments from this study, except for the two-component acetic acid solution, showed positive alteration of the rejection, whereas Laufenberg et al. (1996) reported both positive and negative alteration of RO rejection attributed to intermolecular interactions of aqueous multi-component systems. Specifically, Laufenberg et al. (1996) reported that the presence of butyric acid and oxalic acid increased the rejection of acetic acid by 11.5% and 4.5%, respectively. Therefore, the fermentation broth may collectively improve the rejection of RO membrane.

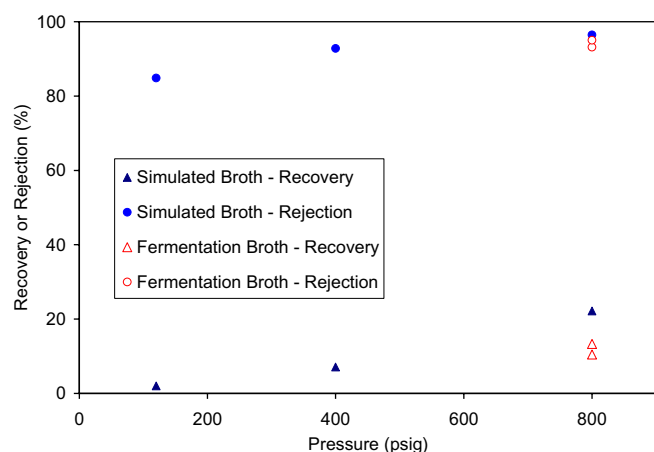


Fig. 8. Comparison of RO performance for simulated and actual fermentation broths.

Fig. 8 shows the results of the overall recovery and rejection in the simulated (six-component) and actual fermentation broths without recirculation of the retentate. Both rejection and recovery for the simulated fermentation broth increased with increasing feed pressure. Recovery ranged from 2% at 120 psig to 22% at 800 psig, whereas rejection increased from 85% at 120 psig to 97% at 800 psig. The overall rejection was calculated by taking the sum of the rejection of six individual model compounds. Two experiments were conducted using the actual fermentation broth at 800 psig. Under these conditions the RO membrane was able to achieve an average 94% rejection of volatile acids and alcohols and 12% recovery of permeate. Again, the rejection was calculated by adding the rejection of the six key components in the fermentation broth. Specifically, the rejections for lactic acid, acetic acid, propionic acid, butyric acid, ethanol, propanol, and butanol were 99.2%, 90.3%, 97.3%, 97.0%, 80.8%, 100%, and 92.3%, respectively. Furthermore, the rejection based on TOC of the fermentation broth was 95.5%, which matched well with the calculated rejection based on the six key components.

Each of the fermentation broth experiments lasted less than one hour due to limited volume of available sample. No fouling of the RO membrane was noticeable over this run time. In a recent study on RO processing of dairy industry effluents, which have some similarity with the fermentation broth, fouling of RO membranes was monitored over the course of 60 h (Turan et al., 2002). It was reported that at a 10,000 mg/L chemical oxygen demand (COD) level, the flux of the RO membranes was reduced by 15% within the first 5 h, and by 60% after 40 h of operation. Therefore, long-term operation issues as well as higher feed temperature conditions, energy consumption, and processing costs will be evaluated in a follow up study.

## 5. Conclusions

This study demonstrated the feasibility of using RO for water reclamation from an anaerobic fermentation broth

obtained from the biohydrogen production process. Using a single cartridge, 150 gal/day commercially available RO system, 95.5% of the TOC in the fermentation broth was rejected. Correlations of rejection and recovery were developed for six model organic compounds, respectively, as a function of feed pressures at 120, 400, and 800 psig, with and without recirculation of the retentate. The rejection was also correlated with molecular weight of the model compounds. The rejection of organic components was consistently enhanced when the simulated mixture or the fermentation broth was used as the feed stream, as compared to processing each component individually. Since metal hydroxide or salt was typically used to control pH at about 5.5 in the fermentation process, the fermentation broth contained high concentrations of dissolved metal ions. This highly dissociated electrolyte solution may have contributed to the improved RO performance. Lactic acid, butyric acid, and butanol were effectively removed with a rejection of greater than 99% at a pressure of 800 psig. Oxalic acid, ethanol and acetic acid were rejected ranging from 79% to 92% at a pressure of 800 psig. Recovery rates as high as 35% of the feed stream were achievable with moderate recirculation.

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